

The Chromium-Iron Equilibrium in Carbides in Steel at 950° C

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
THE UNIVERSITY OF MICHIGAN

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John Franklin Ross

EASTON, PA.:
ESCHENBACH PRINTING COMPANY
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Arbor

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THE CHROMIUM-IRON EQUILIBRIUM IN CARBIDES IN STEEL AT 950° C

Introduction

Chemical reactions and equilibria in highly viscous solvents have received very little attention from chemists up to the present day. In the lesser viscous solvents, such as gases and liquids, many reactions and equilibria have been studied. It is a well-known fact that gases can mix in all proportions to form homogeneous mixtures. Gases to a greater or lesser degree can dissolve in liquids to form perfectly uniform solutions. Almost innumerable solids dissolve in liquids to form homogeneous liquid phases, but the conception that one solid could be completely dispersed or dissolved by another solid, however, seems at first to be beyond our comprehension. This, no doubt, is due to the seemingly prevalent idea that the terms "liquid" and "solution" are more or less synonymous. When the two words are analyzed the fallacy is very evident.

The definition of a solution, as generally accepted, may be stated as follows: a solution is a homogeneous phase which can vary continuously within certain limits. This definition obviously involves no condition as to the physical state of the substances. According to this idea, highly viscous solutions, or in other words, solid solutions, are homogeneous solid phases, the composition of which can undergo continuous variation within certain limits. The range of variation of composition is more limited in the case of liquid solutions than it is in the case of gaseous solutions. The range of miscibility is even more restricted in the case of solids. Examples of complete miscibility, however, are known even in the solid solutions, the Fe-Ni system being a good example of this.

The idea concerning the existence of solid solutions was first suggested by Proust¹ in 1806, when he describes cast iron as a solution of carbides of iron in iron. The solid solution idea was given its first impetus by A. Matthiessen² in 1863. He pointed out that many metals and alloys might be regarded as "solidified solutions" either of miscible liquids or of compounds in solution. Under this conception pure or nearly pure metals would be regarded as liquids or mixtures of liquids, differing from ordinary ones only in viscosity, but still being solvents in which the atomic relations existing between solute and solvent do not differ fundamentally from the same relations in liquid solvents. The fact that Matthiessen used the term "solidified solution" instead of "solid solution" introduces an element of uncertainty as to whether he had the present-day conception of solid solutions or not. He measured the electrical conductivity of various

¹ See *Jr. Iron & Steel Inst.*, 1900, No. 2. Presidential address by Roberts-Austin.

² Report of the British Assoc. for the Advancement of Science, 1863, p. 37.

metals and alloys, but drew no general conclusions as to the relation between chemical constitution and electrical properties.

In 1885, Spring³ brought out an interesting example showing the mutual solubility of solids. He showed that when an equimolecular mixture of barium sulphate and sodium carbonate are pressed together, a double decomposition takes place, which amounts to as much as twenty per cent of the compounds. The fact that an equilibrium is established is only conceivable on the assumption that in the case of these solids we have partial miscibility.

Although the idea of solid solutions had been recognized by metallurgical chemists since the early part of the nineteenth century, it was not until 1890,⁴ due to the work of van't Hoff, that physical chemists adopted the idea and began to develop it along chemical lines.

Roozeboom⁵ introduced the word "Mischkrystalle" in 1891. This term was no doubt suggested to Roozeboom by van't Hoff's work on solid solutions, as he gives full reference to the latter's work. In 1899,⁶ Roozeboom applied the "Mischkrystalle" idea to solid solutions, both components of which are crystalline. The expression "both components" may be somewhat misleading unless we consider the two classes of solid solutions. Certain pairs of metals are isomorphous, that is, they crystallize together in all proportions to form homogeneous crystals, the properties of which vary in a continuous manner from one end of the series to the other. Other pairs of metals, although crystallizing in different forms, are each capable of crystallizing with a small quantity of the second metal, which is thus constrained to take up a crystalline form foreign to it. The term "solid solution" is sometimes retained for the cases in which there is no resemblance of crystalline form, isomorphous mixtures being placed in a separate class, under the heading "mixed crystals." This distinction, however, is not very exacting, and as both cases are considered to be homogeneous phases, it would seem best to group them together under the one term of "solid solution."⁷

The work carried out by Professor E. D. Campbell, in this laboratory, on the constitution of steel, has had for its foundation the solid solution idea, or the validity of the concept of the unity of mechanism of all solutions.

In steel there are elements other than iron and carbon, which are the two essential elements. These other elements may occur as a constituent of the solvent iron or combined with carbon as carbides, with silicon as silicides, with phosphorus as phosphides, etc.

³ *Bull. Soc. Chim.*, **44**, 166 (1885).

⁴ "Ueber feste Lösungen und Molekulargewichtsbestimmung an festen Körpern," *Zeit. phys. Chem.*, **5**, 322 (1890).

⁵ *Zeit. phys. Chem.*, **8**, 504 (1891).

⁶ *Zeit. phys. Chem.*, **30**, 385 (1899).

⁷ See Desch, "Metallography," p. 43.

Object

The object of the present investigation was to determine the equilibrium which would be established in the distribution of chromium between the solute and the solvent, when the carbon concentration alone was varied, the atomic ratios between chromium and iron being kept constant.

Up to the present time no series of steels fulfilling the conditions used in these experiments have been prepared. Commercially it is impossible to cast a series of steels which would vary only in carbon concentration. A series recently described and produced at the Bureau of Standards⁸ involving only iron and carbon, is the only case on record of a series of steels varying only in carbon concentration. The per cent of sulphur in this series varied from 0.003% to 0.02%, and the silicon from 0.002% to 0.039%. Other impurities as well as the sulphur and silicon are negligible. Their series ranged from 0.001% to 1.58% carbon. They also attempted to make a similar series of steels differing in carbon, but containing manganese. In their measurements of physical properties they used steels varying in manganese as much as 0.40% and considered the concentration constant. For their purposes, it was strictly logical to do this, as the variation of manganese made a remarkably small variation of results. It was found next to impossible to prepare a set by a melting process which would have an exact iron to manganese ratio.

Hadfield⁹ prepared a number of alloys of iron and chromium containing from 0.22% to 16.74% chromium and from 0.07% to 2.12% carbon. This is a very fine series, but as the steels were commercially prepared, other elements varied also. The results obtained from the series make a very complete record of the physical properties of chromium steel.

Arnold and Read¹⁰ prepared a very good series of chromium steels. They attempted to maintain the carbon concentration constant and vary only the chromium. The carbon varied from 0.835% to 0.88%, except in one case where the carbon content was 0.64%. The chromium varied from 0.65% to 23.70%. These alloys were commercially cast and the other elements, or impurities, varied to a minor extent.

Preparation of Materials

In order to study the iron-chromium system in solid solution from a more exacting or a chemical viewpoint, it was necessary to prepare a series of chromium steels on a strictly laboratory basis.

The three principles used in the preparation of the series of steels were:

- (1) Carburization of steel by means of a suitable carburizing mixture

⁸ See *Bureau of Standards Scientific Paper*, No. 453.

⁹ *Jr. Iron & Steel Inst.*, 1892, No. 2, p. 49.

¹⁰ *Jr. Iron & Steel Inst.*, 1911, No. 1, p. 249.

- (2) Decarburization of steel with hydrogen
- (3) Equilibrium between high and low carbon steels in hydrogen

A commercial chrome magnet steel furnished by the Penn Seaboard Steel Corporation was used. This steel was machined into small bars about six millimeters square and fifteen centimeters long. Various pieces of the steel were carburized, decarburized, and placed in equilibrium with steel of a different carbon content, thus making a series which varied only in carbon content. It is a well-known fact that when steel is decarburized with hydrogen there is also desulphurization. As the sulphur content in the original steel is only 0.035%, any variation in this amount would be entirely negligible. It has been shown¹¹ that the phosphorus content is not changed by such treatment.

Carburization.—The process of carburizing iron by heating in charcoal has been practised for centuries. It forms the basis of the old cementation process. The principle is used very extensively at the present day to caseharden steels. In the carburization of the steels under consideration, a mixture of 50% wood charcoal, 25% animal charcoal, and 25% barium carbonate, was used. The bars were carefully distributed in this mixture in a cast iron annealing pot, and the cover to the pot was luted on with a mixture of finely ground silica and clay. In order to measure the temperature, a platinum-platinum-rhodium thermocouple was used. The couple was surrounded by a porcelain tube, closed at one end, which extended from the center of the pot through the cover. The bead of the couple was thus placed in the center of the carburizing mixture, and at the same time it was in an oxidizing atmosphere. The means of heating the carburizing system was an electrically-wound vertical tube furnace. The heating chamber of this furnace, which was cylindrical in shape, was about thirty centimeters high and fifteen centimeters in diameter. The annealing pot was placed in the furnace and surrounded with coke screenings or small pieces of charcoal, thus completely filling the heating chamber of the furnace. A layer of asbestos and then one of sheet iron was placed over the coke or charcoal to exclude as much air as possible. The furnace was then heated to about 950° C. and maintained at that temperature from one to three days. It was possible to get a temperature control of $\pm 10^\circ$ C. After the bars had been heated the desired length of time, the current was cut off and the furnace allowed to cool. The mass of the material in the furnace insured rather slow cooling, thus annealing the bars well as they cooled. It required three hours for the furnace to drop the first 200° in temperature, and over a day was required for the system to cool to 80–90° C. If incomplete carburization was desired, the current was reduced before the bars had time to become saturated

¹¹ Campbell, Ross and Fink, *Jr. Iron & Steel Inst.*, 1923, No. 2, p. 179.

with carbon, and the temperature lowered to 800–840° C. and held there for one or two days for diffusion to take place. This made the bars perfectly uniform.

Decarburization.—The principle involved in preparing the decarburized bars is that first described by Campbell¹² in an article on the decarburization of steel with hydrogen. The furnace used for the decarburizations was an electrically heated horizontal tube furnace. The resistance wire was wound on an alundum tube having an outside diameter of about seventy millimeters and an inside diameter of fifty-two millimeters. The portion of this tube encased by the furnace jacket was forty-four centimeters in length. A fused silica reaction tube, having an outside diameter of forty-six millimeters, was used inside the alundum tube. This allowed sufficient space between the two tubes for the insertion of a thermocouple.

The bars to be decarburized were made into the form of a bundle. Thirteen of the six millimeter square bars completely filled the reaction tube. These bars were separated from one another by strands of annealed pure iron wire of small diameter.

The bundle of bars was then placed in the middle of the reaction chamber, which was about forty-four centimeters long. This chamber was then boxed in by means of two small flat-bottomed alundum filtering thimbles to minimize the radiation of heat from the bars.

The hydrogen used in the decarburizations was supplied from a tank of electrolytic hydrogen. When it was desired to use dry hydrogen the gas was passed through a heated tube containing copper gauze, and then through concentrated sulphuric acid, followed by soda lime, before it reached the furnace. By means of a T-tube in the purifying trains and a two-way stopcock at the furnace, it was possible to bubble the hydrogen through water in a Muenche bottle, thus saturating it with water vapor. It was found¹³ in some cases that the moist hydrogen was a more efficient decarburizer than the dry.

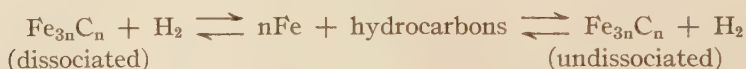
When the furnace and the purifying train were ready for a decarburization experiment, the ends of the fused silica reaction tube, which was thirty-six inches long, were closed with rubber stoppers and suitable stopcocks. The inlet end of the tube was then closed and the tube evacuated by means of a suction pump which was connected at the outlet end. The stoppers were made vacuum tight by applying alternate layers of beeswax and glue. The tube was filled with pure dry hydrogen and re-evacuated, the process being repeated three or four times. The current was then turned on and the furnace brought to a temperature of 950° C. It was possible to maintain this temperature well within 950° C. and 960° C. over any desired length of time. The hydrogen was passed through the

¹² *Jr. Iron & Steel Inst.*, 1919, No. 2, p. 407.

¹³ See Campbell, Ross and Fink, *loc. cit.*

furnace at a rate of about three to four liters an hour. The length of time necessary to complete the decarburizing was about seven days at 950° C. In case moist hydrogen was used, it was necessary to displace all water vapor from the tube. To this end dry hydrogen was passed through the tube for at least one day. The current was then cut and the bars allowed to cool with the furnace. One hour was required for the bars to cool through the first 200° C. and at the end of two hours they were well below the critical range.

Equilibrium in Dry Hydrogen.—The principle involved in this method is that if two solutions, differing widely in carbon concentration, are held in a still atmosphere of pure dry hydrogen at a temperature of about 950° C., that is, well above the upper critical point of pure iron, hydrogen will tend to combine with carbon of the dissociated carbides, removing it in the form of hydrocarbons. These compounds, upon coming in contact with a solution of low carbon content, will react with the iron to form undissociated carbide and hydrogen.



An equilibrium is thus set up between the two carbide concentrations of the two solid solutions and the hydrocarbon concentration in the gas.

In carrying out the equilibria, the same furnace was used as that in which the decarburizations were made. The bars were separated from each other at three points by strands of fine wire, and made into a bundle similar to that used for decarburization. The high and low carbon bars were distributed as uniformly as possible with reference to each other. The bundle was then placed in the furnace and the air in the furnace displaced by pure dry hydrogen by repeated evacuations and fillings. The furnace was maintained under a slight positive pressure of hydrogen, although no hydrogen was allowed to pass through. A Drexel bottle in the purifying train served as a safety valve. The temperature of the furnace was held at 950–960° C. The reaction of the gaseous hydrocarbons is entirely on the surface of the bars and sufficient time must be allowed in order that diffusion will take place, making the bars uniform throughout their entire cross section. It has been shown¹⁴ that this diffusion of the carbides is rather slow in the solid solution, and that for the size bars used, about seven days were required to get a perfectly uniform specimen. After the necessary length of time, the bars were furnace-cooled. The annealing was of the same nature as that obtained when decarburizing samples. It was found that this method was capable of transferring the carbon usually with only about a 5–10% loss.

¹⁴ Campbell, Fink and Ross, *Jr. Iron & Steel Inst.*, 1923, No. 2, p. 173.

Materials Prepared

The steels used in this investigation were prepared from a commercial chrome magnet steel having a carbon content of 0.85%. By the three above mentioned processes, six other concentrations of carbon were prepared. The steels were designated throughout the work by their carbon content and this will be used as a method of identification at this point, although the analyses of the steels have not been discussed.

1.62 Steel.—Eighteen bars of ingot iron (0.015% C) and eight bars of the original chrome steel (0.85% C) were heated in the carburizing mixture for three days at 940–950° C. The bars were furnace cooled.

1.43 Steel.—Four bars of the 1.62 steel and four of the original chrome steel were heated in the equilibrium furnace for seven days at 950° C., the 1.62 steel making the 1.43 steel. The bars were furnace cooled.

1.05 Steel.—This was prepared in the equilibrium of the 1.62 steel with the original chrome steel (0.85%) simultaneous with the 1.43 steel. The 0.85% C steel increased to 1.05% C.

0.85 Steel.—The original chrome steel was heated in Al_2O_3 in a closed pot to 895° C. in the same furnace that was used for carburizing. The bars were then annealed by furnace cooling.

0.50 Steel.—Five bars of the original chrome steel were placed in equilibrium with seven bars of ingot iron (0.015% C) and held at 950° C. for seven days. The bars were allowed to cool with the furnace.

0.36 Steel.—Four bars of the original chrome steel were placed in equilibrium with nine bars of ingot iron (0.015% C) and held at 950° C. for seven days. The bars were then allowed to cool as in the preceding case.

0.04 Steel.—Thirteen bars of the original chrome steel were treated in a stream of pure dry hydrogen at 950° C. for eight days. The carbon content dropped to 0.55–0.60%. Nine of these bars were treated in a stream of pure hydrogen saturated with water vapor for seven days at 950° C. During the last six and one-half hours and throughout the entire cooling period pure dry hydrogen was passed through the tube. The carbon content in this case dropped to 0.04%.

On account of the extremely low carbon content of these bars, no attempt was made at carbide recovery. It would have been almost impossible to obtain sufficient carbides for an analysis.

The methods of preparing and the preparation of some of the bars were worked out with Mr. W. L. Fink. The remainder of the bars were prepared by Mr. G. W. Whitney, assisted by the author.

Analyses of Steels

The complete analysis of the original steel is as follows: C 0.85%, Cr 2.23%, Mn 0.24%, P 0.027%, S 0.035%, Si 0.25%, Ni 0.12%, Cu 0.084%, Fe 96.16%. Only carbon, chromium, manganese and iron were

considered, the latter being determined in every case by difference. In the treatment of the steel the only elements that could vary are carbon and sulphur. Any variation in the sulphur content would be insignificant.

It was found that if the bars were very accurately weighed before treatment and then weighed again after treatment that the gain or loss in weight gave the carbon change. At first thought this method might not appear very reliable, as any oxidation of the bars would cause a gain in weight. It was possible, however, by careful manipulation, to conduct the experiments so as to get no oxidation whatsoever. To illustrate the uniformity of results the computed values on the five bars of 0.50 steel are as follows: 0.489, 0.508, 0.494, 0.491 and 0.515%. In the case of the 1.05 steel, the four bars gave the following results: 1.05, 1.06, 1.04 and 1.07%. These values agree more closely than different analysts can check. In the case of the Bureau of Standards, Electric Steel No. 51, having a certificate value of 1.29% C, the twelve chemists that analyzed it reported from 1.26% to 1.32% C. A few of the steels prepared were checked for carbon by direct combustion and the results by weight were found strictly reliable.

The chromium, manganese, and iron values on the steel were computed on the basis of the new carbon value of the steel. In other words, the steels having a lowered carbon content had necessarily an increase in chromium and iron per cent and the steels having a raised carbon content had a decrease in the percentage of those elements. The calculation factor can be computed as follows: The original 100% of steel minus the carbon content of 0.85% or 99.15% is taken as the unit. If this figure is used as the denominator of a fraction the numerator of the calculation factor can be obtained by taking the plus or minus carbon change from the original

TABLE I
ANALYSES OF STEELS

Steel	Carbon	Chromium	Manganese	Iron	Calc. Factor
0.36	0.36	2.24	0.24	96.63	$\frac{99.64}{99.15} = 1.0049$
0.50	0.50	2.24	0.24	96.50	$\frac{99.50}{99.15} = 1.0035$
0.85	0.85	2.23	0.24	96.16	$\frac{99.15}{99.15} = 1.0000$
1.05	1.05	2.23	0.24	95.97	$\frac{98.95}{99.15} = 0.9980$
1.43	1.43	2.22	0.24	95.60	$\frac{98.57}{99.15} = 0.9942$
1.62	1.62	2.21	0.24	95.41	$\frac{98.38}{99.15} = 0.9923$

0.85% and subtracting or adding these changes from or to the unit 99.15. Table I gives the analyses of the steels and also the factor by means of which they were computed.

Carbide Recovery

The first definite carbide of iron described was that obtained by Sir F. Abel and Mr. Deering,¹⁵ who isolated it by the action of a mixture of dilute sulphuric acid and potassium dichromate on thin sheets of annealed steel. Later Dr. Muller¹⁶ recovered carbides from annealed steel by the action of dilute sulphuric acid. He was able to recover about one-half of the carbon in the steel in the form of carbides. Osmund and Werth¹⁷ treated steel electrolytically in a dilute hydrochloric acid solution and recovered carbides in this manner. Carnot and Goutal¹⁸ used dilute acetic acid in carbide recovery.

In 1896, Campbell¹⁹ recovered a pure carbide of iron by electrolysis in four per cent hydrochloric acid solution. From a study of the gaseous products of the solution of these carbides, a great deal of information as to their structure was brought out. The complexity of the carbides of iron is little realized when the formula Fe_3C is given to them. A far more exacting formula would be Fe_{3n}C_n .

Arnold and Read have done by far the most exhaustive work on carbide recovery. Their first research was done in 1894,²⁰ although they have contributed many pieces of research work along this line since that time. In this first work the straight iron carbon system was considered. They have studied the double carbides of iron and manganese,²¹ keeping the carbon concentration in the steel fairly constant and varying the manganese content. The double carbides of iron and chromium²² were studied by a variation of the chromium content. They also studied the iron-vanadium-carbon²³ system, but in this case both the vanadium and carbon were varied.

In the present investigation, the carbides were recovered electrolytically in a four per cent (40 cc. conc. HCl per liter) solution of hydrochloric acid.

The bars, before electrolysis, were very carefully polished so as to get a smooth surface. It was found that the carbides would tend to flake off if the bars were not perfectly smooth. The bars, as has already been men-

¹⁵ *Proceedings Inst. Mech. Eng.*, **1885**, p. 30.

¹⁶ *Stahl und Eisen*, No. 5.

¹⁷ *Annales des Mines*, **1885**, Vol. 2.

¹⁸ *Comptes Rendus*, **1899**, p. 207.

¹⁹ *Am. r. Chem. Jour.*, **18**, p. 836.

²⁰ *Jour. Chem. Soc.*, **65**, 788 (1894).

²¹ *Jr. Iron & Steel Inst.*, **1910**, No. 1, p. 169.

²² *Ibid.*, **1911**, No. 1, p. 249.

²³ *Ibid.*, **1912**, No. 1, p. 215.

tioned, were about six millimeters square and fifteen centimeters long. Each bar was sawed near one end about halfway through, thus practically making a small hook by means of which the bars could be suspended. The steel was next washed with alcohol, then with ether, and weighed.

The electrolysis was conducted in a tall cylindrical glass jar which was about twelve and one-half centimeters in diameter and twenty-four centimeters high. The cathodes used in the electrolysis were two strips of platinum one centimeter wide and ten centimeters long. The platinum strips were welded to the ends of a platinum wire, so that by making electrical connection to the wire the two cathodes were thus placed in parallel. These cathodes were hung along the sides of the jar and on either side. The bar to be electrolyzed was suspended in the center of the jar by means of a platinum wire connected in the saw cut. Two liters of electrolyte were used to completely cover the suspended bars. By means of a resistance and ammeter in the circuit, the current through the system was adjusted to about 600 milliamperes. The electrolysis was continued for ten to twelve ampere hours. It was found that an ampere hour will dissolve away about one gram of iron and that twelve to fourteen grams of the steel could be dissolved without any danger of the carbides flaking off the bars. In the solution, very little hydrogen was evolved from the bars, showing that the acid action on them was very small. No iron was deposited on the cathodes under the conditions used.

The physical appearance of the bars before and after electrolysis is very similar. The accompanying photographs show the bars before and after electrolysis.

Plate I shows an original bar (No. 52) and one which has been electrolyzed (No. 53).

Plate II shows the same two bars as shown in Plate I with the carbides removed from bar No. 53.

The fact that a piece of steel is so completely filled with a network of carbides is very clearly shown.

When the electrolysis had proceeded a sufficient length of time, the bar was lifted from the electrolyte and placed in a long porcelain boat containing water. By means of a small steel wire brush the adhering carbides were removed from the bar. In the filtration of the carbides a Munroe crucible, that is, a porcelain gooch with platinum sponge filtering mat, was found to be the most satisfactory. The carbides were next transferred to the crucible by means of a jet of water. After washing well with water the carbides were washed with a 2-3% solution of sodium carbonate to remove all traces of acid. The sodium carbonate was then washed out with water, which was in turn removed by absolute alcohol. The carbides were finally washed with ether, care being taken to only remove the excess ether and not draw any air through the carbides. The crucible was

Bar 52

Bar 53

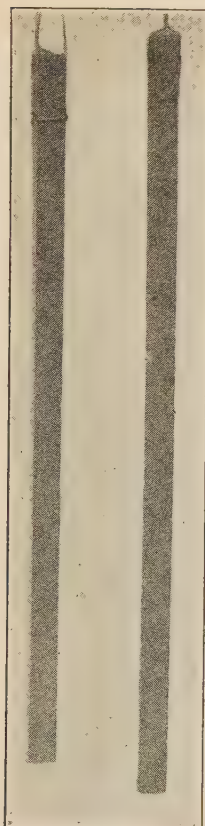


Plate I

Bar 52

Bar 53



Plate II

then placed in a vacuum dessicator containing sulphuric acid, and the carbides allowed to thoroughly dry. The entire operation of removing the carbides from the bars and washing them required less than five minutes' time and there was very little decomposition of the material in this short interval.

In the cases of the 0.36 steel and the 0.50 steel, the carbides recovered were pyrophorus if air was drawn through the crucible containing the carbides which were moist with ether. This tendency to decompose so easily was not present in the hyper-eutectoid steels. The pyrophoric nature in the hypo-eutectoid steels may be due to the extremely fine state of division of the carbides.

When the carbides were dry they were loosened from the bottom of the crucible and all lumps broken up by means of a small stirring rod. After transferring to a weighing bottle they were accurately weighed.

In the cases of the carbides recovered from the hypo-eutectoid steels, there was apparently some oxidation during the crushing process. The carbides seemed to increase slightly in bulk upon being loosened, but there was no temperature change in the crucible. This oxidation amounted to about three and one-half per cent of the weight of the carbides in the case of the 0.36 steel and to about two and one-half per cent in the 0.50 steel. The carbides were weighed in the crucible after standing for about one-half hour in the vacuum dessicator, and it was from these weighings that the above percentages were calculated.

In all cases except the 0.36 steel, one carbide recovery was sufficient. In this case it was necessary to make two recoveries, using about twenty ampere hours of current altogether to get sufficient carbides for analysis.

Physical Appearance.—When viewed under a microscope the carbides appeared to be a very porous, spongy material. They ranged in color from a very dark gray in cases of the lower carbon steels, to a steel gray in the highest carbon steel. When viewed with the naked eye, the carbides all appeared very similar in physical structure up to the 1.62 steel, which appeared somewhat crystalline. This sample of carbides also seemed to be a little more dense than the others.

Magnetic Properties.—Samples of the carbides were placed on a piece of paper on the stage of a microscope. While viewing the carbides, a magnet was passed back and forth under the stage and any movement of the particles was noted. The hypo-eutectoid steels and the 0.85 steel gave carbides which were not attracted by the magnet. The hyper-eutectoid steels gave carbides which were attracted by the magnet and the higher the carbon content of the steel the more magnetic the mass seemed to be.

Analyses of Carbides

Due to the very small quantities of carbides recovered (in some cases less than 500 mg.), it was necessary to determine all the elements on the same sample. Duplicate samples were used in all cases, however.

Carbon.—Two to three hundred milligrams of each of the carbides were weighed in a platinum boat. The carbon was burned to carbon dioxide in a stream of oxygen in a combustion furnace. The furnace was maintained at a low red heat and an oxygen flow of about twelve liters an hour was used. Twenty minutes were allowed to completely flush all carbon dioxide from the tube. Copper oxide was placed in the outlet end of the combustion tube to oxidize any traces of carbon monoxide. The carbon dioxide was absorbed in a Sargent bulb by means of "ascarite," which is a soda lime asbestos mixture. The traces of moisture formed in the reaction of the carbon dioxide with the soda lime were retained in the bulb by magnesium perchlorate, which has been shown²⁴ to be a very efficient dehydrating agent. Very consistent results were obtained, duplicate determinations checking within a few hundredths of one per cent.

The oxide residue from the carbon combustion was then removed from the boat as completely as possible. Any traces of oxide which adhered to the boat were removed by fusion with $K_2S_2O_7$. The oxides with the $K_2S_2O_7$ melt from the boat were then fused with about ten to twelve grams of $K_2S_2O_7$. The solidified melt was placed into a 150 cc. beaker with 75 cc. water and 4 cc. concentrated H_2SO_4 and allowed to digest over night on a low temperature hot plate. This long period for solution was necessitated by the slight solubility of the basic chromium salts formed. Any traces of residue remaining in the beaker after the over night treatment were filtered off and refluxed with $K_2S_2O_7$. These residues were tested for silica by means of hydrofluoric acid, and none was found. This would indicate that silicides in the steel are completely oxidized, the silicon going into solution as silicic acid during the electrolysis.

Manganese.—The completed solution of the oxides was diluted to 100 cc. in a volumetric flask calibrated by means of ten deliveries from a 10 cc. pipette. By means of this pipette one-tenth of the sample was drawn off for use in determining the manganese. To this 10 cc. of solution, 5 cc. of syrupy H_3PO_4 , 2 cc. concentrated H_2SO_4 and 200–300 mg. of KIO_4 were added. The solution was then diluted to about 75 cc. and boiled to oxidize the manganese of $HMnO_4$. After dilution to 100 cc. in a volumetric flask, the solutions were compared in a colorimeter by means of a standard permanganate solution. It was found that by the addition of 2 mg. of chromium to the standard, the comparisons were more easily made.

Chromium.—In order to separate the chromium and iron the Na_2O_2

²⁴ Smith, Brown and Ross, *J. I. E. C.*, **16**, 20 (1924).

fusion method was found to be very unsatisfactory. Due to this fact a new procedure was devised. The method used for the chromium-iron separation is, to the best of the author's knowledge, original. It consisted in oxidizing the chromium to the dichromate by means of $(\text{NH}_4)_2\text{S}_2\text{O}_8$. The solution was then poured into a solution of $(\text{NH}_4)_2\text{HPO}_4$ and the iron present precipitated as FePO_4 . After filtration the chromium was titrated in the filtrate. This method gave results which checked to within one to two hundredths of a per cent. When the size of the sample (about 250 mg.) is taken into account, the accuracy of the method is very remarkable.

The procedure was as follows: To the chromium-iron solution, having a volume of about 150 cc., a drop of AgNO_3 solution and about 2 g. of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ were added. The solution was boiled for at least twenty minutes to oxidize the chromium and remove the excess persulphate. It was found that no manganese would oxidize to permanganic acid until all the chromium was oxidized to dichromate. Thus, in order to insure complete oxidation of the chromium, the process of adding $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and boiling was continued until the permanganate color appeared. Two or three drops of HCl were added to reduce the permanganic acid and boiling continued until all persulphate was destroyed. The solution, having about a 100 cc. volume, was then cooled and poured into 150 cc. of a solution of 10 g. NaOH and 5 g. $(\text{NH}_4)_2\text{HPO}_4$, which had just been prepared. If the solution was not alkaline at this point it was made so by the addition of a slight excess of NH_4OH . Paper pulp was added to prevent the FePO_4 from running through a filter, and the solution was boiled. After settling, the FePO_4 was filtered out and washed with cold water containing an electrolyte. The process of filtration was not particularly rapid, but more so than a $\text{Fe}(\text{OH})_3$ filtration. The filtrate was made acid by about 5 cc. of concentrated H_2SO_4 , and titrated electrometrically with standard FeSO_4 . The electrometric end-point, no doubt, attributed a great deal to the accuracy of the method.

Iron.—The moist FePO_4 precipitate was dissolved off the filter paper by means of hot 1:5 H_2SO_4 . The acidity of the solution was adjusted by means of NaOH so as to have an acid concentration of about 1–2 cc. of concentrated H_2SO_4 per 100 cc. of solution. The FePO_4 solution was

TABLE II
ANALYSES OF CARBIDES

Steel	Carbon	Chromium	Manganese	Iron	Total %
0.36	7.38	20.70	0.76	54.02	82.86
0.50	7.73	18.23	0.76	58.92	85.64
0.85	6.73	15.01	0.76	71.18	93.68
1.05	6.81	11.44	0.61	75.33	94.19
1.43	6.82	10.08	0.56	78.44	95.90
1.62	6.65	8.06	0.55	83.11	98.37

then drawn through a Jones reductor and the iron titrated with standard KMnO_4 .

The weight per cents of C, Cr, Mn and Fe in the carbides as recovered are given in Table II.

Data Obtained From Electrolysis

In Table III are given the weights of carbon, chromium, manganese, and iron removed from the different steels, computed from the per cent of these elements as shown in Table I and the loss of weight of each bar during the electrolysis.

TABLE III

TOTAL WEIGHT OF ELEMENTS, C, CR, MN, AND FE REMOVED FROM THE BARS BY ELECTROLYSIS

Steel	Total	Carbon	Chromium	Manganese	Iron
0.36	20.5808	0.0741	0.4610	0.0494	19.8872
0.50	11.7386	0.0587	0.2630	0.0282	11.3277
0.85	14.0549	0.1195	0.3134	0.0337	13.5152
1.05	14.1513	0.1486	0.3156	0.0340	13.5800
1.43	12.9124	0.1846	0.2867	0.0310	12.3443
1.62	13.5801	0.2200	0.3001	0.0326	12.9567

In Table IV are given the weights of carbon, chromium, manganese and iron recovered as carbides, computed from the percentage of these elements in the carbides as shown in Table II, and the total weight of carbides recovered.

TABLE IV

TOTAL WEIGHT OF ELEMENTS, C, CR, MN, AND FE RECOVERED AS CARBIDES

Steel	Total	Carbon	Chromium	Manganese	Iron
0.36	0.5494	0.0405	0.1137	0.0042	0.2968
0.50	0.3941	0.0305	0.0718	0.0030	0.2322
0.85	1.3910	0.0936	0.2088	0.0106	0.9901
1.05	1.5869	0.1081	0.1815	0.0097	1.1954
1.43	1.8840	0.1285	0.1899	0.0106	1.4778
1.62	3.3036	0.2197	0.2663	0.0182	2.7456

The weights of carbon, chromium, manganese and iron, not recovered as carbides, computed by subtracting the weights given in Table IV from the totals given in Table III are shown in Table V.

TABLE V

TOTAL WEIGHT OF ELEMENTS, C, CR, MN, AND FE, NOT RECOVERED AS CARBIDES

Steel	Total	Carbon	Chromium	Manganese	Iron
0.36	20.0314	0.0336	0.3473	0.0452	19.5904
0.50	11.3445	0.0282	0.1911	0.0252	11.0955
0.85	12.6639	0.0259	0.1046	0.0232	12.5251
1.05	12.5644	0.0405	0.1340	0.0243	12.3846
1.43	11.0284	0.0562	0.0968	0.0204	10.8665
1.62	10.2765	0.0003	0.0338	0.0144	10.2111

Computation of Data to Atomic and Unit Basis

In order to reduce all results to a uniform basis for comparison, a so-called "unit" weight of steel was adopted. Since, in the series of steels prepared, the concentration of carbon alone was varied while the relative weights of chromium, manganese, and iron remained constant, the "unit" weight of steel adopted was that weight of each steel which contained one hundred milligram atoms of chromium, manganese, and iron together. These "unit" weights were computed from the weight per cents of these elements as given in Table I.

Calculation of "Unit" Weight.—If the weight per cents of chromium, manganese and iron in the original steel are divided by their corresponding atomic weights, the results will give the relative atomic concentrations of the three elements. The relative ratios thus obtained are then reduced to a 100% basis of the three elements. The atomic ratios thus found in the original steel were: Cr 2.44, Mn 0.24 and Fe 97.32. Multiplying each of these ratios by the atomic weight of the corresponding element in milligrams gives the weight of each of these elements in one unit of steel. Dividing the sum of these three weights by the sum of the weight per cents of the three elements in the steel gives the weight of steel necessary to contain one hundred milatoms of the three elements. This latter weight has been termed the "unit" weight for each steel.

These values, together with the number of "unit" weights dissolved in the electrolyses, are given in Table VI.

TABLE VI
"UNIT" WEIGHTS

Steel	"Unit" weight of steel	"Unit" weights dissolved
0.36	5.624	3.659
0.50	5.632	2.084
0.85	5.652	2.487
1.05	5.663	2.499
1.43	5.685	2.272
1.62	5.696	2.384

The total weight of carbides and contained carbon, chromium, manganese and iron recovered per "unit" weight of each steel is given in Table VII.

TABLE VII
TOTAL CARBIDES AND CONTAINED C, CR, MN, AND FE RECOVERED PER "UNIT" WEIGHT
OF STEEL DISSOLVED

Steel	Total carbides	Carbon	Chromium	Manganese	Iron
0.36	0.1502	0.0111	0.0311	0.0011	0.0811
0.50	0.1891	0.0146	0.0344	0.0014	0.1114
0.85	0.5593	0.0376	0.0840	0.0042	0.3981
1.05	0.6350	0.0432	0.0726	0.0039	0.4783
1.43	0.8292	0.0566	0.0836	0.0046	0.6504
1.62	1.3857	0.0921	0.1117	0.0076	1.1517

In Table VIII are shown the number of milligram atoms of carbon in one "unit" weight of each of the steels, together with the constant 100 milatoms of accompanying chromium, manganese and iron. From this table the relative atomic concentrations of chromium to carbon in each of the steels can be readily computed.

TABLE VIII
MILATOMS OF C, CR, MN, AND FE PER "UNIT" WEIGHT OF STEEL

Steel	Carbon	Chromium	Manganese	Iron
0.36	1.687	2.44	0.24	97.32
0.50	2.347	2.44	0.24	97.32
0.85	4.004	2.44	0.24	97.32
1.05	4.955	2.44	0.24	97.32
1.43	6.775	2.44	0.24	97.32
1.62	7.690	2.44	0.24	97.32

In Table IX are given the milatoms of carbon, chromium, manganese and iron recovered as carbides per "unit" of steel dissolved.

TABLE IX
MILATOMS OF C, CR, MN, AND FE RECOVERED AS CARBIDES PER "UNIT" WEIGHT OF STEEL

Steel	Carbon	Chromium	Manganese	Iron
0.36	0.924	0.598	0.021	1.453
0.50	1.218	0.663	0.026	1.995
0.85	3.137	1.614	0.077	7.129
1.05	3.604	1.397	0.070	8.565
1.43	4.713	1.607	0.085	11.648
1.62	7.679	2.148	0.139	20.623

Table X is obtained by subtracting the values given in Table IX from the corresponding ones in Table VIII and consequently it shows the number of milatoms of each of the four elements not recovered as carbides.

TABLE X
MILATOMS OF C, CR, MN, AND FE NOT RECOVERED AS CARBIDES, PER "UNIT" WEIGHT OF STEEL

Steel	Carbon	Chromium	Manganese	Iron
0.36	0.763	1.84	0.22	95.87
0.50	1.129	1.78	0.21	95.32
0.85	0.867	0.83	0.16	90.19
1.05	1.351	1.04	0.17	88.75
1.43	2.062	0.83	0.15	85.67
1.62	0.011	0.29	0.10	76.70

In Table VIII the milatoms of chromium, manganese and iron in one "unit" weight of steel are given, being computed in atom per cents of the three elements, and are constant for all the steels. In order to get a correct idea of the influence of changes in carbon concentration in the steels on the relative proportion of chromium to manganese to iron in the car-

bides, the milatoms of each of the three elements recovered as carbides, as shown in Table IX, have been computed to a similar basis and expressed in the form of atom per cents of the three metals. These ratios are given in Table XI.

TABLE XI
ATOMIC PER CENTS OF CR, MN, FE IN CARBIDES RECOVERED

Steel	% Chromium	% Manganese	% Iron
0.36	28.86	1.01	70.13
0.50	24.70	0.97	74.33
0.85	18.30	0.87	80.83
1.05	13.93	0.70	85.37
1.43	12.05	0.64	87.31
1.62	9.37	0.61	90.02

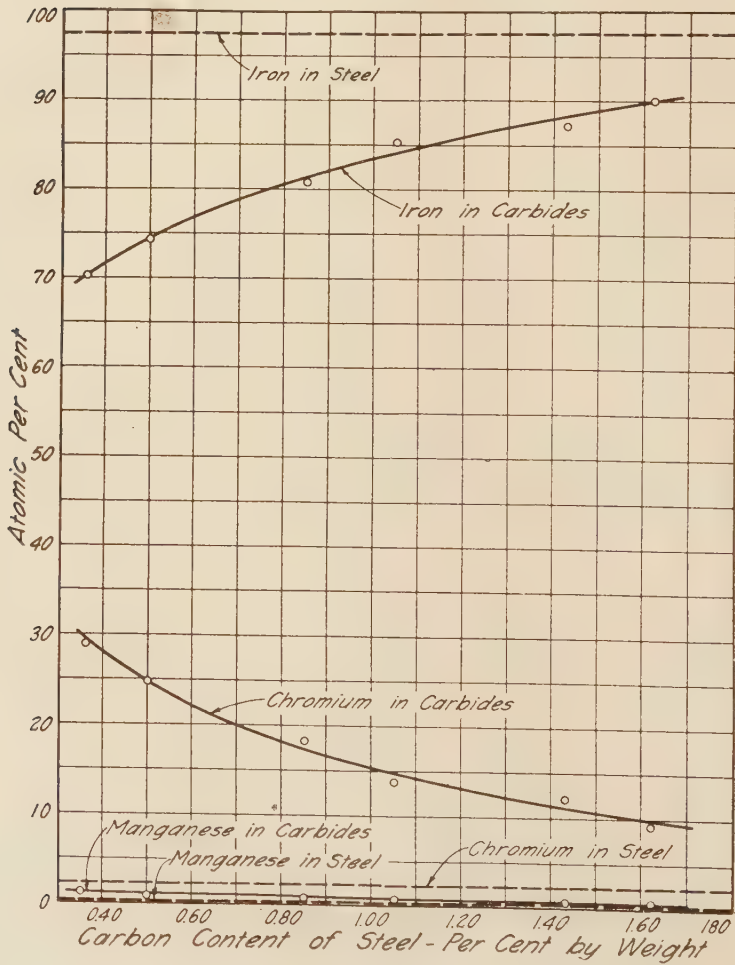


Plate III

The atomic ratios of chromium, manganese and iron in both the steel (Table VIII) and the carbides (Table XI) are shown graphically in Plate III.

In Table XII are given the atomic ratios of chromium to carbon in the steels (from Table VIII) and the atomic ratios of chromium to carbon in the carbides and chromium to iron in the carbides computed from Table IX.

TABLE XII
ATOMIC RATIOS

Steel	$\frac{\text{Cr}}{\text{C}}$ in steel	$\frac{\text{Cr}}{\text{C}}$ in carbides	$\frac{\text{Cr}}{\text{Fe}}$ in carbides
0.36	1.446	0.647	0.412
0.50	1.040	0.545	0.332
0.85	0.609	0.515	0.226
1.05	0.492	0.387	0.163
1.43	0.360	0.341	0.138
1.62	0.317	0.280	0.104

The data given in Table XII are shown graphically in Plate IV in which the atomic ratios of chromium to carbon in the steel are used as abscissa, while the atomic ratios of chromium to carbon and chromium to iron in the carbides are used as ordinates.

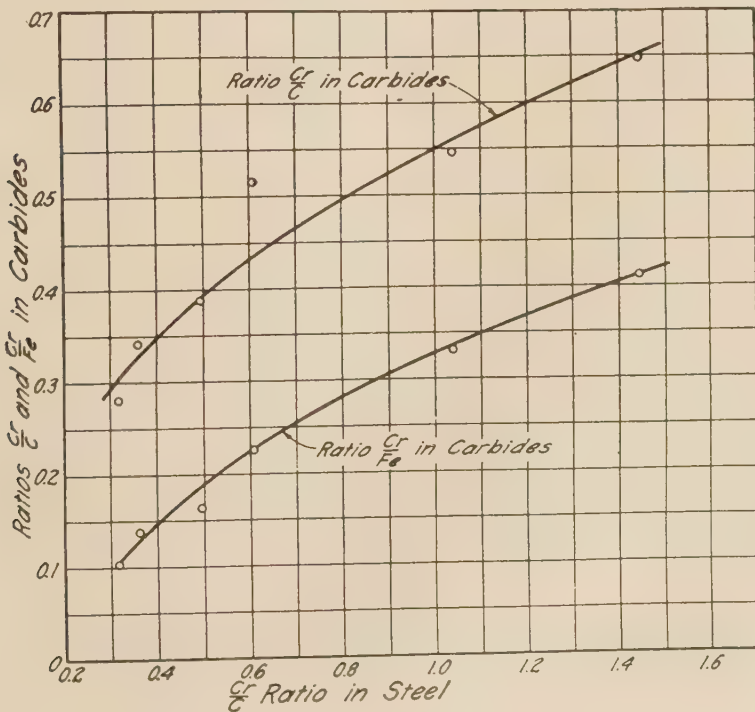


Plate IV

Discussion and Summary of Results

In the following discussion it will be noticed:

(1) The total weight of carbides recovered from "unit" weight of steel increases with the carbon concentration of the original steel. (See Table VII, column 2.)

(2) The size of the precipitated carbide particles, and hence the extent to which they will be dissolved during electrolysis or "not recovered," will depend upon the rate of annealing of the steels. In the cases of the 0.36, 0.50, 1.05 and 1.43 steels, less than two hours were required for the bars to cool through the critical range, whereas in the cases of the 0.85 and 1.62 steels about three times as long a time was required for cooling to the same extent.

(3) In the cases of the "medium" annealed steels (0.36, 0.50, 1.05 and 1.43) the milatoms of carbon "not recovered" increase with increase in total carbon in the steel, while in the "slow" annealed steels (0.85 and 1.62) the milatoms of carbon "not recovered" is markedly less in the 0.85 steel and almost zero in the 1.62 sample. (See Table X, column 2). In order to obtain a comparison of the solubility in α -iron of the carbides of a hypoeutectoid chrome steel with those of a very pure carbon steel, carbides were recovered from a 0.45% C bar of such steel. The two steels compared were annealed at the same rate. The carbon "not recovered" from the pure carbon steel was 0.18 milatoms per 100 milatoms of iron, while that "not recovered" from the 0.50 steel was 1.129 milatoms per 100 milatoms of metal. It will thus be seen that the carbides from the chrome steel are about six times as soluble in α -iron as those from the pure carbon steel.

(4) In the cases of the "medium" annealed steels, the milatoms of chromium "not recovered" decrease as the total carbon in the steel increases. The effect of slow annealing is to diminish the loss of chromium as compared with that which would be found for medium annealed bars of the same total carbon content. (Table X, column 3.)

(5) Although the manganese content of the steel is quite low in the original metal, the tendency of manganese to concentrate in the carbides in a manner similar to that of chromium is clearly shown in Table IX, column 4.

(6) A study of the curves given in Plates III and IV seem to indicate quite clearly that the laws governing the distribution of chromium between solute and solvent are analogous to those which hold in the formation of mixed crystals or solid solutions in aqueous solutions or in fused salts.

Conclusion

The results of the present investigation add further evidence to the probability of the idea of the unity of mechanism of all solutions.

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